L1: Entry 1 of 4   File: USPT   Apr 19, 2005

DOCUMENT-IDENTIFIER: US 6881336 B2
TITLE: Spiral wound element with improved feed space

Brief Summary Text (4):
Pressure-driven membrane separation processes allow a broad range of neutral and
ionic species to be removed from fluids. In order of decreasing pore size,
membranes are commonly classified into several categories: microfiltration (MF),
ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Microfiltration
is used for removal of suspended particles having particle sizes greater than 0.1
microns. Ultrafiltration commonly excludes dissolved molecules having molecular
weights greater than 5,000 daltons. Nanofiltration membranes pass at least some
salts but usually have high retention of organic compounds having molecular weights
greater than approximately 200 daltons. Reverse osmosis membranes have high
retention of almost all species.

Brief Summary Text (5):
An alternative means of characterizing membranes is by their method of formation.
MF and UF membranes can be made by a wide variety of techniques and commercially
significant methods include etching, sintering, partial fracture by stretching, and
phase-inversion. NF and RO membranes are generally made by either phase inversion
or interfacial polymerization. Interfacial polymerization results in a composite
structure having a very thin discriminating layer with high selectivity affixed to
a porous support and it is by far the dominate procedure for creating NF and RO
membranes. Interfacial polymerization can be performed with a wide variety of
monomers as is described in U.S. Pat. No. 6,337,018 incorporated herein in its
entirety by reference.

Brief Summary Text (6):
NF and RO membranes are most commonly used in applications such as desalination of
seawater or brackish water, production of ultrapure water, color removal, waste
water treatment, and concentration of liquids for food products. A critical factor
in almost all NF and RO applications is that the membrane achieve high rejection of
small solute molecules while maintaining high flux.

Brief Summary Text (7):
A spiral wound element is the most common configuration for RO and NF membranes. A
classic spiral wound element design is illustrated in FIG. 1. "Feed" liquid flows
axially through a feed spacer sheet and exits on the opposite end as "concentrate".
"Permeate" passes under pressure through membrane envelopes and is directed to a
permeate collection tube by a permeate carrier sheet. In comparison to alternative
configurations (hollow-fiber, plate-and-frame, and tubular modules), spiral wound
elements often have a favorable combination of low cost, low polarization, and low
pressure drop across the element.

Brief Summary Text (8):
Element performance can be further enhanced with optimal element design. For
example, it is possible to simultaneously vary the number of envelopes in an
element and their lengths to optimize efficiency. For the same element diameter,
increasing the number of envelopes in an element results in less active area since
more envelopes means more inactive end regions. However, increasing envelope length

(as measured in the direction perpendicular from the axis of collection tube)
results in greater pressure drop within the longer permeate carrier sheets and this
can also decrease element flow during operation. (An increased pressure drop within
the permeate carrier sheets results in less flux--flow per unit of membrane area.)
For a given set of conditions, the optimal trade-off between envelope length and
the number of membrane envelopes can be made to maximize flow. The same trade-off
also impacts solute rejection which is maximized for element designs with a larger
number of envelopes and shorter individual envelope lengths. Assuming knowledge of
several parameters including expected operating conditions, the required element
diameter, the active width of membrane envelopes and the thickness of element
materials (feed spacer, permeate carrier, and membrane), the impact of trade-off
between flow and rejection can be predicted and optimized.

Brief Summary Text (9):
Spiral wound elements are usually placed inside of a cylindrical pressure vessel
for operation. While there are exceptions, makers of spiral wound elements and the
vessel that enclose them have converged on a few standard dimensions. Nominal
diameters of 50 mm, 60 mm, 100 mm and 200 mm are most common for RO/NF elements.
Elements having 60 mm diameter are usually available as approximately 350 mm, 530
mm, or one meter long, measured along the axis from the ends of slightly extended
permeate collection tubes. Elements with diameters of 100 mm or 200 mm are usually
available only in a one meter length. Vessels are created to hold an integral
number of these elements in series. One reason for these standard element lengths
is that the industry has commonly made membrane with a width of approximately one
meter and the stated lengths allow for efficient use of this membrane. The permeate
carrier and feed spacer sheets can be also be cut efficiently from meter wide
rolls. Assigning the axial dimension of a spiral wound element to be an integral
fraction of one meter allows the length of individual membrane envelopes to be
unconstrained by materials.

Brief Summary Text (10):
In commercial RO and NF applications, a large filtration system may be composed of
more than 10,000 elements, usually distributed in pressure vessels containing 4 to
7 elements each. The pressure vessels have ports for inputting the pressurized feed
solution and removing the concentrate and permeate solutions. Feed flows axially
through each of the elements in series. By connecting the permeate collection tubes
of different elements, the effect is to create one long element in a vessel. Each
pressure vessel can be further combined in series or parallel with other vessels to
create a filtration system. A filtration system can be operated with re-circulation
where concentrate is re-pressurized and allowed to pass several times through a
vessel or in `single-pass` mode, where solution passes only once through any
portion of the system. Large single-pass filtration systems are typically arranged
in a tapered design where the concentrate from several upstream vessels feeds a
smaller number of downstream vessels. While such systems may achieve high recovery
with high cross flow, they are also characterized by a long continuous feed path
and high pressure drop. System design can be further complicated by incorporating a
variety of other options, including booster pumps, permeate pressurization, and
cascading stages. Appropriate system design allows the desired recovery and
permeate quality to be achieved, and many of the available options are described
and illustrated in Marcel Mulder, "Basic Principles of Membrane Technology",
Chapter 8, Kluwer Academic Publishers, Dordrecht, The Netherlands, (1991).

Brief Summary Text (11):
Separation efficiency in RO or NF spiral wound elements is dictated by pressure and
concentration gradients across the membrane. The flux (volumetric flow per unit
area of membrane) of the solvent (most often water) is generally proportional to
the net-driving pressure. This net-driving pressure is defined as the difference in
feed and permeate applied pressures minus the osmotic pressure differential across
the membrane. Solvent flux goes down for high solute concentration and low
transmembrane pressure. By contrast, solute molecules commonly pass through RO and

NF membrane based on diffusion and this process is ideally driven by a
concentration gradient and not affected substantially by the pressure gradient. As
a consequence, the concentration of a well-rejected solute in the permeate is
inversely proportional to the net-driving pressure.

Brief Summary Text (12):
The net-driving pressure of an element can be influenced by the pressure drop
between the fluid entrance end of a spiral wound element and the exiting end. In
operation, a feed solution under pressure is applied to the entrance end of the
spiral wound element and it flows axially through the cylindrical element. The
resulting pressure drop depends on the volume of feed flowing through the element
and the resistance of the feed spacer sheet to this flow. This pressure drop is
less (usually much less) than the net-driving pressure. A typical pressure drop
across a one meter long RO/NF element would be about 25 kPa when the feed has a
superficial velocity of 15 cm/sec in the channel. The superficial velocity may be
defined as the volumetric flow divided by the cross sectional area of an empty
channel. For a standard commercially available Film Tec.TM. 200 mm diameter (8
inch) element with 35 m.sup.2 (380 ft.sup.2) of membrane, the 15 cm/sec corresponds
to about 200 m.sup.3 /day of feed solution. Pressure drop is approximately linear
with flow rate.

Brief Summary Text (13):
In a series of elements such as in a vessel, the first element in series operates
with higher net-driving-pressure than those at the downstream end resulting in an
uneven distribution of flux. One cause for the difference is the fact that feed
concentration increases in successive elements resulting in more osmotic pressure.
This effect is augmented (and sometimes overshadowed) by the pressure drop down a
series of elements. There are several problems with this inhomogeneous utilization
of membrane. For the lead elements, high flux can substantially shorten the life of
an element due to fouling and scaling. High flux also promotes concentration
polarization and polarization decreases the effective rejection of the membrane.
Lower flux in the trailing elements is also undesirable, not only because of
decreased productivity, but also because lower flux means higher solute
concentration in the permeate.

Brief Summary Text (15):
Ideally, the problem of pressure drop would be addressed at the source--the feed
spacer sheet. Unfortunately, the selection of an optimal feed spacer sheet can be a
complex task as several key aspects of the feed spacer sheet are difficult to
predict from its structure. In addition to having low resistance to feed flow so as
to maintain low pressure drop across the element, the ideal feed spacer would also
have other characteristics. The primary purpose of the feed spacer is to separate
two membrane sheets, allowing the feed solution to flow across their front
surfaces. Towards that end, the ideal permeate spacer sheet (also referred to as
"spacer", "net" or "spacer sheet") would have a high density of contacts points
with the membrane so that nesting of membrane envelopes is avoided. Nesting results
when the contact points of adjacent envelopes become offset during rolling and
deformation of the two envelopes decreases a spacer's effective volume. Ideally,
the spacer would be thin so that it does not greatly decrease the amount of
membrane area that can be packed into an element of a given diameter; it would
promote substantial mixing so that solute polarization at the surface of the
membrane is small; it would have a smooth surface so as not to damage the
discriminating layer of the membrane with which it is in contact; and of course it
would also be inexpensive to manufacture and use.

Brief Summary Text (16):
Designing an optimal feed spacer is a balancing of competing concerns. For
instance, increasing a spacer's thickness results in less pressure drop but
conflicts with the desire to maximize an element's active membrane area. Another
important conflict stems from the desire for reduced concentration polarization

within an element. Concentration polarization is a phenomena resulting in a higher concentration of solute at the membrane's surface than in the bulk. It is caused by the membrane's selectivity. During operation, solutes in the feed solution are continually driven to the membrane surface by convective transport of the feed. In the absence of mixing, rejected solutes must be removed from the surface by diffusion. Coupling competing mass transfer processes to axial flow results in the solute concentration at the membrane's surface increasing down the length of the channel. The effect is especially important for large solute molecules, high permeate fluxes and low feed velocities in the axial direction. The increased concentration at the membrane's surface results in both decreased permeation of water (due to osmotic pressure, scaling, gel formation or fouling) and increased passage of solute molecules (caused by a greater effective concentration). One purpose of a feed spacer is to cause localized regions of turbulence, breaking up the build-up of polarization. Unfortunately, energy required for mixing at the membrane's surface must necessarily contribute to energy dissipation through the element (pressure drop).

Brief Summary Text (17):
In further regard to pressure drop, two key characteristics of the feed spacer are its thickness (height of the channel) and its void fraction. When the volume of liquid flowing through the spacer is kept constant, increasing either property will generally cause a decrease in pressure drop. The pressure drop of a "net-type" spacer oriented along the flow direction, as shown in FIG. 2, is further characterized in Da Costa, Fane, & Wiley, J. Membrane Science, 87, 79-98 (1994), where formulas recognize its dependence on several geometric characteristics: thickness, void fraction, mesh size, filament diameter, and the angle between filaments. The interrelations between these parameters are recognized and for a constant void fraction, the paper demonstrated the impact of trading mesh size and hydrodynamic angle. (The hydrodynamic angle is defined here as the angle, formed between two filaments, which faces the channel axis.) It was found that when flow, thickness, and void fraction are kept constant, decreasing the hydrodynamic angle resulted in a smaller pressure drop down the flow channel. At the same time a lower hydrodynamic angle (at the same void fraction) resulted in a greater mesh size and a dramatic decrease in mixing, parameterized by the mass transfer coefficient.

Brief Summary Text (19):
In Da Costa, Fane, Fell, & Franken, J. Memb. Science, 62, 275-291 (1991), feed spacer sheets at different orientation were examined during the filtration of dextran through an ultrafiltration membrane. The study used several commercial feed spacers but extra configurations were obtained by varying their orientation in the channel or by removing cross strands to increase void fraction. It was found that the minimum operating cost was obtained with a feed spacer having a hydrodynamic angle of about 80.degree.. A second study, Da Costa, Fane, & Wiley, (1994), more fully characterized these spacers according to geometric characteristics and developed a semi-empirical model for pressure drop that accounted for different sources of energy dissipation. The trade-off between pressure drop and mass transfer was detailed and the model was used to predict optimal net configurations. Predictions confirm the previous experimental results but also elaborated on the ranges of optimal angle and void fraction for ultrafiltration under different flow conditions. At low cross flow velocities it was concluded that a net-type spacer should combine low void fraction (about 0.4) with a hydrodynamic angle between 50.degree. and 120.degree.. A third study by the same authors (Da Costa & Fane, Ind. Eng. Chem. Res., 33, 1845-1851, (1994) found that the size and location of filaments positioned perpendicular to flow was particularly important to mass transfer. Under the conditions examined it was concluded that UF elements would have better mixing and would produce more flow when spacers composed of perpendicular filaments were oriented so that one set of filaments was perpendicular to the flow direction, as compared to when both sets of filaments were oriented at 45.degree. to the channel axis.

Brief Summary Text (20):
In Polyakov & Karelin, J. Membrane Science, 75, 205-211, (1992), a different set of feed spacers were examined for filtration of sodium chloride through reverse osmosis composite membranes. The authors introduced a model for polarization that was dependent on the angle between filaments and the feed flow direction. It was hypothesized that regions between filaments corresponded to developing turbulent flow and that the periodic blockage of membrane by filaments caused regions of polarization attenuation. Based on examination of different spacers, including two that are similar to those used in commercial RO elements, they found the best configuration had a filament angle of 63.5.degree. to the flow direction. This traversing angle is equivalent to a 127.degree. hydrodynamic angle, as previously defined.

Brief Summary Text (21):
In Zimmerer & Kottke, Desalination, 104, 129-134, (1996) the authors examined flow through biplanar spacers formed by stacking two layers of grid rods at different angles. Using flow visualization techniques they characterized two extremes of flow types and related them to two parameters: the traversing angle and the dimensionless mesh size. (The dimensionless mesh size was defined as the mesh size divided by the filament diameter.) Channel flow was found to dominate when the angle was low and the mesh size was short, resulting in poor mixing. `Corkscrew flow` dominated at the other extreme and it resulted in poor mass transfer between neighboring stream paths. The authors suggested that the two domains can be overlapped by appropriate choices for the angle and dimensionless wavelength allowing a "perfect mixing" that results in homogenous use of the membrane surface. A preferred spacer, based on this mixing criteria, had a hydrodynamic angle of 120.degree. and a dimensionless mesh size of 5.5.

Brief Summary Text (24):
Nitto Denko's JP 05168869 describes an element constructed using a net having one set of filaments parallel to the feed flow direction and the other set of filaments crossing the flow direction at an angle less than 80.degree.. More preferably, this angle is between 20.degree. and 50.degree.. Examples provided use a 0.35 mm thick net having traversing angles of either 25.degree. and 40.degree.. The better of the two spacers demonstrated a pressure loss of about 76 kPa/m for a feed flow rate 15 cm/sec. The described spacer had the particular disadvantage of being asymmetric, so that the two surrounding membranes sheets each will see a different hydrodynamic environment. Also, as pointed out in EP 1029583, this spacer requires advanced net-making techniques when compared to the current art.

Brief Summary Text (25):
Feed spacers for commercial NF and RO elements have been characterized in several sources (e.g. G. Schock, A. Miquel, "Mass transfer and pressure loss in spiral wound modules, Desalination, 64, 339 (1987); S. V. Polyakov and F. N. Karelin, "Turbulence promoter geometry: its influence on salt rejection and pressure losses of a composite-membrane spiral wound module" J. Memb. Sci., 75, 205, (1992)). These are commonly made with a net-type feed spacer having an average thickness of between 0.5 and 2 mm, a perpendicular spacing between filaments of between 1 and 4 mm, a void fraction near 0.9, and a hydrodynamic angle about 90.degree.. The net is oriented so that the flow direction bisects this angle, resulting in a traversing angle of 45.degree.. In the Zimmerer paper, different configurations were studied through construction of spacer sections from stacked grid rods, using several hydrodynamic angles other than 90.degree.. In the Da Costa articles, flow through nets having a variety of different configurations were examined by rotating or modifying existing netting. The Toray patent applications used webs having a variety of hydrodynamic angles. Several patents (U.S. Pat. No. 4,022,692, U.S. Pat. No. 4,861,487, U.S. Pat. No. 4,902,417) also describe low pressure-drop, asymmetric nets, having one filament set oriented parallel to the flow direction. Despite these studies, commercial manufacture of nets for RO/NF elements are still very dominated by the standard 90.degree. netting and a 45.degree. traversing angle,

with limitations imposed by both convention and legitimate processing concerns.

Brief Summary Text (33):
The present invention relates to a spiral wound membrane element with an improved feed spacer sheet and to methods for making and using the same. Consistent with commercially available designs, the feed spacer of the subject element comprises a net having a first set of mutually substantially parallel filaments crossed with a second set of mutually substantially parallel filaments. The improved feed spacer of this invention has a high degree of strand thinning characterized by a narrowing of filaments in the region between crossing points. A measurement of strand thinning for a region between neighboring crossing points is calculated by dividing the effective filament thickness by the corresponding minimum filament width (in the plane of the net).

Drawing Description Text (3):
FIG. 1 is a perspective, partially cutaway view of a spiral wound element. The element is formed by alternately wrapping filtration envelopes and feed spacer sheets about a central permeate collection tube. The filtration envelop comprises a permeate carrier sheet sandwiched between two sheets of membrane.

Detailed Description Text (2):
The spiral wound element is the dominant design for incorporating a large quantity of RO or NF membrane into a small volume. The construction of spiral wound elements has been described in more detail elsewhere (see U.S. Pat. Nos. 5,538,642 and 5,681,467 incorporated herein by reference). A classic spiral wound element design is shown in FIG. 1. Such elements are formed by wrapping one or more membrane envelopes (2) and feed spacer sheet (4) about a central permeate collection tube (6). The envelopes (2) comprise two generally rectangular membrane sheets (8) surrounding a permeate carrier sheet (10). This "sandwich" structure is commonly held together by adhesive (12) along three edges (14,16,18), although several other means exist to seal the three envelope edges. The fourth edge (20) of the envelope (2) abuts the permeate collection tube (6) so that the permeate carrier sheet (10) is in fluid contact with openings (22) in the permeate collection tube (6). Each envelope (2) is separated by feed spacer sheet (4) that is also wound about the collection tube (6). The feed spacer (4) is in fluid contact with both ends of the element (24,26) and it acts as a conduit for feed solution across the front surface (28) of the membrane (8). the direction of feed flow (30) is from the entrance end (24) to the concentrate end (26) and this direction is parallel to the axis (32) of the central permeate collection tube (6).

Detailed Description Text (7):
When parameters of extrusion are not known, the same formula may be used after separating individual strands and determining the mass of polymer comprising the two types. The typical diameters may also be estimated from visual inspection of the web. In the present invention, the typical filament diameters are preferably between 0.15 and 0.6 mm. Also preferably, diameters are the same for both sets of substantially mutually parallel filaments (34,36) allowing for similar mixing at the surfaces (28) of facing membrane sheets (8).

Detailed Description Text (9):
The thickness of a net used in the present invention is preferably between 0.25 and 1 mm. Decreased thickness results in greater pressure drop, more propensity to foul, and a likelihood for uneven flow within the element. Increasing the thickness of the net reduces the active area of membrane that can be packed into an element. Increasing net thickness also decreases the superficial velocity of fluid that moves through the channel for a given volumetric flow rate, and this worsens polarization.

Detailed Description Text (10):
The mesh size (46,48) is the distance between filament crossing points,

corresponding to the length of sides for the typical parallelogram (44). A very related measurement is the strand spacing (58,60), defined as the perpendicular distance between filaments of a set. The preferred net would have strand spacing values between 1 and 5 mm for both sets of filaments. When strand spacing (58,60) of the feed spacer (4) increases, nesting of adjacent envelopes (2) during element rolling becomes a problem and this nesting increases pressure drop. Additionally, it is thought that low strand spacing and low mesh size improve polarization resulting in more frequent regions of turbulent flow. At the other extreme, when strand spacing and mesh size are too small, pressure drop increases and the net is more difficult to produce. It is not necessary that strand spacing be identical for both sets of filaments but this is preferable since it is desirable that mixing at the front surfaces (28) of facing membrane sheets (8) be similar.

Detailed Description Text (16):
In the spiral wound element of this invention, the hydrodynamic angle (56) is less than 70.degree., more preferably less than 60.degree., and most preferably less than 55.degree.. The net is oriented such that the hydrodynamic angle (56) is approximately bisected by the flow direction. By "approximately bisected" it is meant that the line bisecting the hydrodynamic angle (56) is within 10.degree.of parallel to the permeate collection tube (6). In this way, both sets of filaments (34,36) make approximately the same traversing angle (52,54) with the direction of feed flow (30) through the element. As noted also with filament diameter and strand spacing, the resulting symmetry allows two facing sheets of membrane (8) to have similar polarization and results in homogeneous utilization of membrane area. For purposes of this disclosure, a symmetric feed spacer is one in which both sets of filaments have approximately equal strand spacing (58,60), typical diameter and traversing angle (52,54).

Detailed Description Text (19):
The prediction of mass transfer for the purpose of spacer design is complicated and stretches the limit of current computing power. To a large extent, the improvement in passage can be understood in terms of the high flux obtained with low pressure drop. However, literature suggests that lower hydrodynamic angles (56) are expected to substantially worsen polarization. While it is not be meant to be limiting to the invention, an explanation may be proposed for the favorable mixing observed with this spacer despite its lower hydrodynamic angle (56). One explanation is that stagnant regions caused by direct contact with the membrane front surfaces (28) are avoided by the suspended, stretched filaments. This is in contrast with earlier experimental results (Feron, Desalination, 84, 1991, 137-152) that suggest mixing is less effective for suspended rods than for rods attached to a membrane's surface, but that study was performed with much larger structures (both filaments and channels) where dynamics may be different. An alternative explanation is that strand thinning maintains a high void volume while allowing more frequent interruptions in developing polarization, due to close strand spacing (58,60).

Detailed Description Text (27):
A flat cell having a length of 914 mm, a width of 127 mm and a channel depth of 1.27 mm was loaded with membrane, feed spacer sheet, and the appropriate shims to fill the channel's free space. The feed spacer described above was oriented such that the flow direction was perpendicular to the machine direction, resulting in a hydrodynamic angle of 50.7.degree.. Water at 25.degree. C. was caused to flow through the cell while maintaining a recovery of less than 5%. The pressure drop across the feed spacer sheet was measured as a function of superficial feed velocity. Results are shown in FIG. 4, along with those from Comparative Example I.

Detailed Description Text (37):
Four FilmTec.TM. NF270-4040 spiral wound element were fabricated using standard feed spacer sheet, similar to that in Comparative Examples II and III. The commercial NF270-4040 elements are approximately one meter long and 100 mm in

diameter, and they contain 7.0 m.sup.2 of active <u>membrane</u> area. Eight additional elements of the same design were constructed using different feed spacer sheet. Four contained the feed spacer of Example I and four contained the feed spacer of Example II. In each case, the machine direction of the net was perpendicular to the central collection tube.

<u>Detailed Description Text</u> (40):
The feed spacers of Example II and Comparative Example I were run in the presence of 100 ppm NaCl on the 914 mm long flat cell. The orientation of feed spacers in the flat cell was the same as described previously. Using FilmTec.TM. <u>NF90</u> <u>membrane,</u> performance properties (flux, salt passage, and pressure drop) were recorded when operating the system at 140 kPa and a superficial feed velocity of 32 cm/sec. This data is provided in Table III, and it shows that the new net compares favorably with conventional material.

<u>Other Reference Publication</u> (1):
Da Costa et al., "Optimal Channel Spacer Design For Ultrafiltration," Journal of <u>Membrane</u> Science, vol. 62, Elsevier Science Publishers B.V., Amsterdam, 1991, pp. 275-291.

<u>Other Reference Publication</u> (3):
Da Costa, et al., "Spacer Characterization and Pressure Drop Modeling in Spacer-Filled Channels for Ultrafiltration," Journal of <u>Membrane</u> Science, vol. 87, Elsevier Science Publishers B.V., Amsterdam, 1994, pp. 79-98.

<u>Other Reference Publication</u> (4):
Farkova, "The Pressure Drop in <u>Membrane</u> Module With Spacers," Journal of <u>Membrane</u> Science, vol. 64, Elsevier Science Publishers B.V. Amsterdam, 1991, pp. 103-111.

<u>Other Reference Publication</u> (6):
Karelin and Polyakov, "Turbulence Promoter Geometry: Its Influence On Salt Rejection and Pressure Losses of a Composite-<u>Membrane</u> Spiral Wound Module," Journal of <u>Membrane</u> Science, vol. 75 Elsevier Science Publishers B. V., Amsterdam, 1992, pp. 205-211.

<u>Other Reference Publication</u> (9):
Mulder, Basic Principles of <u>Membrane</u> Technology, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1991 Chapter 8, "Module and Process Design," pp. 312-351.

CLAIMS:

1. An improved spiral wound element having: a central collection tube defining an axis and having a plurality of openings along its length to receive permeate; at least one filtration envelope extending outwardly from and wound about said tube, said filtration envelope comprising two sheets of <u>membrane</u> and a permeate carrier sheet sandwiched between said sheets of <u>membrane</u>; said permeate carrier sheet being in direct fluid communication with said openings of said collection tube; at least one feed spacer sheet wound about said collection tube, said feed spacer sheet being in planar contact with the outer surface of at least one filtration envelope; wherein the improvement is characterized in that said feed spacer sheet is a net comprising a first set of substantially parallel filaments crossed with a second set of substantially parallel filaments to form a plurality of parallelograms having an acute angle less than 70.degree., said net oriented such that a line bisecting said acute angle is approximately parallel to the axis of the central collection tube, and wherein said net has a strand thinning parameter greater than 1.3.

9. An improved spiral wound element having: a central collection tube with a plurality of openings along its length to receive permeate; at least one filtration

envelope extending outwardly from and wound about said tube, said filtration
envelope comprising two sheets of membrane and a permeate carrier sheet sandwiched
between said sheets of membrane; said permeate carrier sheet being in direct fluid
communication with said openings of said collection tube; at least one feed spacer
sheet wound about said collection tube, said feed spacer sheet being in planar
contact with the outer surface of at least one filtration envelope; wherein the
improvement is characterized in that said feed spacer sheet is a net comprising a
first set of substantially parallel filaments crossed with a second set
substantially parallel filaments to form a plurality of parallelograms, said net
having a strand thinning parameter greater than 1.6.

Hit List

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☐ 1.   Document ID: US 6881336 B2

L1: Entry 1 of 4   File: USPT   Apr 19, 2005

US-PAT-NO: 6881336
DOCUMENT-IDENTIFIER: US 6881336 B2

TITLE: Spiral wound element with improved feed space

DATE-ISSUED: April 19, 2005

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Johnson; Jon E.	Plymouth	MN		

US-CL-CURRENT: 210/321.76; 210/321.74, 210/321.85, 210/650, 210/652, 428/105, 428/114, 96/11, 96/4

| Full | Title | Citation | Front | Review | Classification | Date | Reference | | | | Claims | KWIC | Draw De |

☐ 2.   Document ID: US 6573364 B1

L1: Entry 2 of 4   File: USPT   Jun 3, 2003

US-PAT-NO: 6573364
DOCUMENT-IDENTIFIER: US 6573364 B1

TITLE: Isolation and characterization of Hermansky Pudlak Syndrome (HPS) protein complexes and HPS protein-interacting proteins

DATE-ISSUED: June 3, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Nandabalan; Krishnan	Guilford	CT		
Yang; Meijia	East Lyme	CT		

US-CL-CURRENT: 530/350; 435/317.1

| Full | Title | Citation | Front | Review | Classification | Date | Reference | | | | Claims | KWIC | Draw De |

☐ 3.   Document ID: US 6335170 B1

L1: Entry 3 of 4   File: USPT   Jan 1, 2002

US-PAT-NO: 6335170
DOCUMENT-IDENTIFIER: US 6335170 B1

TITLE: Gene expression in bladder tumors

DATE-ISSUED: January 1, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Orntoft; Torben F.	DK 8230 Aabyhoj			DK

US-CL-CURRENT: 435/6; 435/91.1, 435/91.2, 536/23.1, 536/24.3, 536/24.31, 536/24.33

| Full | Title | Citation | Front | Review | Classification | Date | Reference | | | Claims | KWIC | Draw De |

☐ 4.   Document ID: US 5994076 A

L1: Entry 4 of 4   File: USPT   Nov 30, 1999

US-PAT-NO: 5994076
DOCUMENT-IDENTIFIER: US 5994076 A

TITLE: Methods of assaying differential expression

DATE-ISSUED: November 30, 1999

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Chenchik; Alex	Palo Alto	CA		
Jokhadze; George	Mountain View	CA		
Bibilashvilli; Robert	Moscow			RU

US-CL-CURRENT: 435/6; 435/91.1, 435/91.2, 536/23.1, 536/24.3, 536/24.31, 536/24.33

| Full | Title | Citation | Front | Review | Classification | Date | Reference | | | Claims | KWIC | Draw De |

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Terms	Documents
membrane and "nf90"	4

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L2: Entry 2 of 5   File: USPT   Dec 3, 2002

DOCUMENT-IDENTIFIER: US 6488847 B2
** See image for Certificate of Correction **
TITLE: Process and equipment for recovering developer from photoresist development
waste and reusing it

Brief Summary Text (7):
Meanwhile, waste discharged from the development step of using an aqueous TAAH
solution as the alkali developer in the photolithographic process (called
"photoresist development waste" and hereinafter often referred to in brief as
"development waste") usually contains the dissolved photoresist and TAAH, and is
hard to render harmless through any treatments. Thus, it is desired to recover and
reuse TAAH because of its adverse effects on environment, and various attempts have
been made to develop a method of recovering and rejuvenating an alkali developer
(hereinafter often referred to as "developer"). Examples of such a method include
methods comprising electrodialysis or electrolysis (Japanese Patent Laid-Open No.
7-328642 published on Dec. 19, 1995, and Japanese Patent Laid-Open No. 5-17889
published on Jan. 26, 1993), a method using an anion exchange resin (Japanese
Patent Laid-Open No. 10-85741 published on Apr. 7, 1998), a method comprising
electrodialysis or electrolysis and using an ion exchange resin(s) (U.S. Pat. No.
5,874,204 patented on Feb. 23, 1999), a method comprising neutralization and
electrolysis (Japanese Patent Laid-Open No. 7-41979 published on Feb. 10, 1995), a
method using activated carbon (Japanese Patent Laid-Open No. 58-30753 published on
Feb. 23, 1983), and a method using a nanofiltration membrane (NF membrane)
[Japanese Patent Laid-Open No. 11-192481 published on Jul. 21, 1999].

Brief Summary Text (13):
In the conventional methods of recovering and reusing a TAAH-containing developer,
however, part or the whole of any surface-active substances including the
photoresist component is removed. This will be described below in connection with
individual unit operations usable in these methods. (1) Since surface-active
substances such as a photoresist and a surfactant, even if endowed with an electric
charge, are hardly concentrated in either electrodialysis or electrolysis because
these comparatively high molecular weight substances do not migrate through a
diaphragm such as an ion exchange membrane. This is particularly true of nonionic
surface-active substances, which migrate such a diaphragm only slightly by
diffusion. (2) A surface-active substance having an electric charge is removed by
an ion exchange resin. (3) Surface-active substances are generally adsorbed on
activated carbon. (4) Surface-active substances are removed into concentrate with a
nanofilter because they are high in molecular weight.

Brief Summary Text (23):
Various methods can be mentioned as the method of separating impurities such as
photoresist from a development waste to recover a TAAH solution. Preferred is a
method comprising subjecting the development waste to at least one step selected
from among a concentration and refining step (A) of concentrating and refining TAAH
by at least one of electrodialysis and electrolysis (Japanese Patent Laid-Open No.
7-328642 and Japanese Patent Laid-Open No. 5-17889, incorporated herein by
reference in their entirety), an ion exchange treatment step (B) of contact
treatment with an anion exchanger (preferably an anion exchange resin desirably in
the OH form in an aspect of refining) or with the above-mentioned anion exchanger

and a cation exchange resin in one of the H form and the TAA form (Japanese Patent Laid-Open No. 10-85741 and U.S. Pat. No. 5,874,204, incorporated herein by reference in their entirety), and an NF membrane separation treatment step (C) of obtaining permeate mainly containing TAAH by treatment with a nanofiltration membrane (NF membrane) [Japanese Patent Laid-Open No. 11-192481, incorporated herein by reference in its entirety once laid open although it has not yet been published]. When a plurality of such steps are taken, the order thereof may be arbitrary, and any proper order thereof may be chosen, for example, in accordance with the purpose. The steps (A), (B) and (C) can all remove impurities as steps of refining the development waste or a TAAH-containing treated solution derived therefrom. Among them, the step (B) in particular is a desirable step for removing impurities as much as possible, and the step (A) can concentrate TAAH.

Brief Summary Text (25):
Where a plurality of such concentration methods are used in combination, the order thereof is not particularly limited but may be arbitrary. For example, however, when reverse osmosis membrane treatment and/or evaporation is followed by electrodialysis and/or electrolysis, there can be obtained advantages such as an improvement in current efficiency during electrodialysis and/or electrolysis, miniaturization and running cost reduction of an electrodialysis and/or electrolysis unit(s) due to a decrease in the amount of the solution to be treated therewith, lowering of a voltage to be applied to such a unit(s), and an improvement in TAAH recovery (U.S. Pat. No. 5,874,204). When the ion exchange treatment step (B) and/or the NF membrane separation treatment step (C) is also taken in this case, this evaporation and/or reverse osmosis membrane treatment step may be taken at any stage, e.g., at first, later or between both. Incidentally, since either condensed water obtained by evaporation or permeate water obtained by reverse osmosis membrane treatment does not substantially contain the photoresist and TAAH, the water can be used as process water or the like. In the case of reverse osmosis membrane treatment, the solution to be treated thereby preferably has a pH value of 9 to 12 from the standpoint of minimizing the deterioration of a reverse osmosis membrane.

Brief Summary Text (28):
The NF membrane separation treatment step (C) may be taken in multiple stages (Japanese Patent Laid-Open No. 11-192481). In the step (C), concentrate mainly containing impurities such as photoresist is obtained together with permeate mainly containing TAAH. The NF membrane to be used in the step (C) is a separation membrane having a molecular cutoff falling within the range of 100 to 1,000 and characterized by a sodium chloride rejection of at most 90% when a 0.2% (wt./vol.) aqueous solution of sodium chloride as a solution to be treated is subjected to separation treatment with the membrane at 25.degree. C.

Brief Summary Text (29):
When the development waste or a TAAH-containing solution derived therefrom is treated with the NF membrane, most of TAAH permeates through the NF membrane to enter the permeate, while little or a little photoresist permeates through the NF membrane to remain mostly in the concentrate, wherein the photoresist is therefore concentrated. Further, some impurities such as metal components including Fe and Al, and silica, which are hard to remove in the ion exchange treatment step (B), can be removed into the concentrate because they little permeate through the NF membrane.

Brief Summary Text (30):
Since the permeate stripped of most of impurities is obtained in the NF membrane separation treatment step (C), the load of impurities can be decreased in any later step(s) such for example as the ion exchange treatment, electrodialysis and/or electrolysis step, if taken, to reduce the refining cost. Incidentally, the NF membrane separation treatment step (C) is inexpensive and easy of operation.

Brief Summary Text (32):
Other methods of separating impurities such as photoresist from a development waste
to recover a TAAH solution include methods wherein a development waste is subjected
to a neutralization+solid-liquid separation step, a step of decomposing organics
with ozone, hydrogen peroxide or ultraviolet ray irradiation, and an electrolysis
concentration step in this order (Japanese Patent Laid-Open No. 4-41979 published
on Jul. 12, 1992, Japanese Patent Laid-Open No. 5-17889 published on Jan. 26, 1993,
and Japanese Patent Laid-Open No. 5-106074 published on Apr. 27, 1993, incorporated
herein by reference in their entirety), and a method wherein a development waste is
subjected to a neutralization+solid-liquid separation step and an electrolysis
concentration step in this order. In such cases, most of the photoresist is removed
by neutralization+solid-liquid separation, and a TAA salt formed by neutralization
turns back to TAAH with the aid of electrolysis. When the purity of the TAAH-
containing solution obtained by any method as mentioned above is insufficient, at
least one of the aforementioned steps (A), (B) and (C), the chelate resin treatment
step, and so on may be taken as a later step(s). When the TAAH-containing solution
is low in TAAH concentration, an evaporation and/or reverse osmosis <u>membrane</u>
treatment step may be taken as a later step(s).

Brief Summary Text (34):
As shown in FIG. 9, cation exchange <u>membranes</u> 103 and anion exchange <u>membranes</u> 104
are arrayed alternately with each other between a cathode 101 and an anode 102 to
form a plurality of cells. TAAH in a starting solution (development waste or TAAH-
containing solution derived therefrom) containing TAAH and photoresist (R), and
sent to the cells dissociates into TAA ions (TAA.sup.+) as cations and OH ions as
anions. When a DC electric current is applied between the cathode 101 and the anode
102, therefore, TAA ions are transferred toward the cathode across a cation
exchange <u>membrane</u> 103 but substantially blocked by an anion exchange <u>membrane</u> 104
next thereto, while OH ions are transferred toward the anode across an anion
exchange <u>membrane</u> 104 but substantially blocked by a cation exchange <u>membrane</u> 103
next thereto. Thus, TAAH is concentrated in a given cell, while TAAH is depleted in
cells adjacent to that cell. More specifically, a cell (A) having an anion exchange
<u>membrane</u> 104 facing the cathode 101 functions as a concentrating cell wherein TAAH
is concentrated to form concentrate, while a cell (B) having an anion exchange
<u>membrane</u> 104 facing the anode 102 functions as a desalting cell wherein TAAH is
depleted to form a desalted solution. Since the photoresist (R) in the starting
solution hardly moves across the ion exchange <u>membranes,</u> the photoresist (R) is
passed substantially as such through every concentrating cell and every desalting
cell to remain in the concentrate and the desalted solution.

Brief Summary Text (36):
Where a high-purity TAAH solution reutilizable as a photoresist alkali developer is
to be regenerated and recovered, a concentrate not substantially containing various
impurities is preferably obtained through electrodialysis. For that purpose, it is
preferred that (ultra)pure water or a solution of an electrolyte such as a low-
concentration TAAH solution free of various impurities (e.g., a solution prepared
by dissolving a small amount of virgin TAAH in pure or ultrapure water) be passed
through the concentrating cells while passing the starting solution through the
desalting cells. Where the starting solution is passed through the concentrating
cells as well, however, an advantage is gained in respect of a decrease in the
amount (volume) of wastewater discharged as desalted waste. In order to obtain a
high-purity TAAH solution with a decrease in the amount of wastewater discharged as
desalted waste, there also is preferably used such a method that permeate obtained
by treating the starting solution containing TAAH and photoresist with an NF
<u>membrane</u> be sent to concentrating cells while sending the starting solution or
concentrate obtained through treatment thereof with the NF <u>membrane</u> to desalting
cells. In any case, the desalted solution obtained by electrodialysis may be used
as a source of photoresist as a surface-active substance either as such or after
proper refining treatment thereof such as ion exchange resin treatment and/or
chelate resin treatment if necessary.

Brief Summary Text (37):
The electrodialysis unit may be one as is generally used. Examples of ion exchange membranes to be used in this unit, though not particularly limited in so far as capable of selectively separating either cations or anions, include ACIPLEX (registered trademark of products manufactured by Asahi Chemical Industry Co., Ltd.), SELEMION (registered trademark of products manufactured by Asahi Glass Co., Ltd.), NEOSEPTA (registered trademark of products manufactured by Tokuyama Soda Co., Ltd.), IonClad (registered trademark) electrically driven separation membranes (manufactured by Pall Company), and Nafion (registered trademark of products manufactured by E. I. du Pont de Nemours and Company). Properties of ion exchange membranes may be typical.

Brief Summary Text (38):
The structure of the electrodialysis unit is not particularly limited. For example, a plurality of cation exchange membranes and a plurality of anion exchange membranes may be stacked alternately with each other while maintaining appropriate intervals therebetween with gaskets provided either with an inflow port and an outflow port for a desalting solution, or with an inflow port and an outflow port for a concentrating liquid to form a plurality of cells, which are interposed between a pair of electrodes to construct an electrodialyzer.

Brief Summary Text (39):
The electrodialysis unit is not limited to the above-mentioned typical structure, but may alternatively be constructed in such a way that bipolar membranes are each disposed as diaphragms between the cation exchange membranes and the anion exchange membranes, for example, as disclosed in Japanese Patent Laid-Open No. 6-299,385 published on Oct. 25, 1994 (incorporated herein by reference in its entirety).

Brief Summary Text (41):
Herein, neutral membranes such as polyvinyl alcohol membranes or hydrophilized porous Teflon (registered trademark of products manufactured by E. I. du Pont de Nemours and Company) membranes, which have a superior alkali resistance to that of anion exchange membranes, may be used instead of the anion exchange membranes. The neutral membranes, which are simple polymer membranes free of ionic functional groups, allow TAA ions to pass thereacross, but are lower in permeability thereto than cation exchange membranes. In this case, therefore, a difference in transference number between the neutral membranes and the cation exchange membranes is taken advantage of, whereby TAA ions can be concentrated by electrodialysis. When the neutral membranes are used instead of the anion exchange membranes, however, the current efficiency is worse than that in the case of the anion exchange membranes.

Brief Summary Text (44):
As shown in FIG. 10, a cation exchange membrane 123 is disposed between a cathode 121 and an anode 122 to form a cathode cell (C) and an anode cell (D). In principle, the cation exchange membrane allows only cations to pass thereacross [actually, however, anions including photoresist (R.sup.-) and the like are slightly passed thereacross]. A starting solution (development waste or TAAH-containing solution derived therefrom) is passed through the anode cell (D), while (ultra)pure water, a solution of an electrolyte such as a low-concentration TAAH solution free of various impurities (e.g., a solution prepared by dissolving a small amount of virgin TAAH in pure or ultrapure water), or the like is passed as a concentrating liquid through the cathode cell (C). Since TAAH in the starting solution dissociates into TAA ions (TAA.sup.+) and OH ions (OH.sup.-), TAA ions as cations are transferred toward the cathode (-) to enter the cathode cell (C) across the cation exchange membrane 123 when a DC electric current is applied between the cathode 121 and the anode 122. On the cathode 121, hydrogen ions (H.sup.+) from water (H.sub.2 O.rarw..fwdarw.H.sup.+ +OH.sup.-) receive electrons (e.sup.-) to generate hydrogen gas (H.sup.+), while residual OH ions (OH.sup.-) as anions become

counter ions of TAA ions entering the cathode cell (C) from the anode cell (D) to form TAAH. Thus, TAAH is concentrated in the cathode cell (C) in keeping with progress of electrolysis. In this sense, the cathode cell (C) functions as a concentrating cell. On the other hand, on the anode 122, OH ions (OH.sup.-) of TAAH release electrons (e.sup.-) to become oxygen gas (O.sub.2) and water. In this sense, the anode cell (D) functions as a desalting cell wherein a desalted solution ("dilute solution" depleted of TAA ions) is formed.

Brief Summary Text (46):
Additionally stated, if ionic species such as Cl.sup.- or Br.sup.-, which is more liable to undergo electrolysis than OH.sup.-, is contained in the starting solution, a gas such as Cl.sub.2 or Br.sub.2 is generated. In this case, further division of the anode cell with an anion exchange membrane with addition of an alkaline substance such as ammonium hydroxide to a sectional cell on the anode's side can prevent generation of a gas such as Cl.sub.2 or Br.sub.2 through neutralization as disclosed in Japanese Patent Laid-Open No. 57-155390 published on Sep. 25, 1982 (incorporated herein by reference in its entirety). On the other hand, SO.sub.4.sup.2- and NO.sub.3.sup.- undergo electrolysis less easily than OH.sup.-, so that they remain in the form of H.sub.2 SO.sub.4, HNO.sub.3, etc. with electrolysis of OH.sup.- involving generation of O.sub.2.

Brief Summary Text (47):
Two neutral membranes such as hydrophilized porous Teflon membranes may alternatively be used instead of the cation exchange membrane to provide an anode chamber, a middle chamber and a cathode chamber, wherein electrolysis can be effected by passing the starting solution through the middle chamber (Japanese Patent Laid-Open No. 60-247641 published on Dec. 7, 1985, incorporated herein by reference in its entirety).

Brief Summary Text (48):
When a higher-purity TAAH concentrate is desired to be obtained, a plurality of (preferably two) cation exchange membranes may be disposed between the cathode and the anode. In this case, the starting solution is passed through a cell on the anode's side (anode cell), while a concentrating liquid (liquid for recovery therein of TAAH) such for example as (ultra)pure water or a solution of an electrolyte such as a low-concentration TAAH solution free of various impurities (e.g., a solution prepared by dissolving a small amount of virgin TAAH in pure or ultrapure water) is passed through a cell on the cathode's side (cathode cell) and the middle cell, whereby TAAH can be refined in multiple stages to obtain a high-purity TAAH concentrate from the cathode cell.

Brief Summary Text (58):
Examples of the NF membrane that may be used in the step (C) include NTR-7410, NTR-7450, NTR-725HF, NTR-7250, NTR-729HF, and NTR-769SR manufactured by NITTO DENKO CORPORATION; SU-200S, SU-500, and SU-600 manufactured by Toray Industries, Inc.; NF-45, NF-55, NF-70, and NF-90 manufactured by FilmTec Corporation; DESAL-5L and DESAL-5K manufactured by Desal Co. Limited; TS-80 manufactured by TrySep Corporation; TFC-S manufactured by Fluid Systems; and MPF-34, MPF-36, MPT-34, MPT-36, MPS-34 and MPS-36 of Sel RO (registered trademark) series manufactured by Koch Membrane Systems, Inc.

Brief Summary Text (59):
An NF membrane having a surface thereof charged negative is preferably used as a membrane principally aimed at separation and removal of photoresist into the concentrate. Since the photoresist usually exists in the anionic form in the development waste or the TAAH-containing treated solution derived therefrom [e.g., TAAH-containing solution treated in the step (A) and/or (B)], the use of the NF membrane having a surface thereof charged negative improves the rejection against the photoresist and hardly brings about fouling (contamination) of the NF membrane otherwise attributed to attachment thereto of the photoresist. In this case, an

anionic surfactant, when contained in the development waste or the TAAH-containing treated solution derived therefrom, can also be effectively separated and removed into the concentrate. Further, in general, the NF membrane is also capable of separating and removing a nonionic surfactant, a cationic surfactant, etc. into the concentrate. Needless to say, an NF membrane having a surface thereof charged positive or a neutral NF membrane may also be used in accordance with properties of the development waste or the TAAH-containing treated solution derived therefrom (e.g., the kind of surfactant, if contained therein). The concentrate containing the photoresist and/or a surfactant and thus separated with the NF membrane may be used as a source of surface-active substance either as such or after proper refining treatment thereof such as ion exchange resin treatment and/or chelate resin treatment if necessary.

Brief Summary Text (60):
In general, the NF membrane is comparatively weak against a high-pH solution. In order to prolong the life span of the NF membrane, the pH of a solution to be treated therewith is desired to be adjusted to a value of 9.5 to 12 if necessary, and preferably to a value of 9.5 to 11, to which the pH is, however, not limited in so far as the use of the NF membrane is well costeffective. It is preferred to provide a safety filter of at most 25 .mu.m in pore size in front of the NF membrane in order to avoid a fear of clogging of the NF membrane with fine impurity particles and the like. This applies at whatever stage the step (C) of separation with the NF membrane is taken. Care must also be taken because the increasing TAAH concentration of the solution being treated with the NF membrane raises the operating pressure of a nanofilter and shortens the life span of the NF membrane with an increase in pH.

Brief Summary Text (63):
For example, when a refining step(s) such as the ion exchange treatment, electrodialysis and/or electrolysis step is taken, it is preferred that such a step (s) be taken after the step (C) of separation with the NF membrane, if taken, rather than before the step (C) from the standpoint of decreasing the load on a refining unit(s) for use in such a refining step(s) because the purity of the NF permeate is considerably high. For example, in the case where the step (C) is aimed at removing a slight amount of impurities (particularly some metal components including Fe and Al, and silica, which are hard to remove by ion exchange treatment, and the like), however, the refining step(s) such as the ion exchange treatment, electrodialysis and/or electrolysis step may be taken before the step (C). Needless to say, such refining steps may optionally be taken both before and after the step (C). In the case where the impurity concentration of the original development waste is low, in the case where the use of the rejuvenated developer is such that a low purity thereof is tolerable, or in the like case, the NF permeate may alternatively be subjected to at least one of evaporation, reverse osmosis membrane treatment, electrodialysis and electrolysis for concentration of TAMH, and/or to adjustment of the TAAH concentration by addition thereto of a virgin conc. TAAH solution, or the like after the step (C) without ion exchange treatment.

Brief Summary Text (67):
When the chelate resin and the ion exchange resin are used for heightening the purity of a TAAH solution in the course of obtaining the rejuvenated developer, use of an NF membrane in advance thereof is preferred in order to lower the load on the chelate resin and the ion exchange resin. An NF membrane may be used after use of the chelate resin and the ion exchange resin for the purpose of further heightening the purity of a TAAH solution.

Brief Summary Text (71):
A membrane treatment unit may further be provided at or near the terminal of the system for carrying out the present invention. In this case, fine particles that exist in the development waste from the beginning, and fine particles that may mix

therein from pumps, an electrodialysis and/or electrolysis unit, a chelate resin,
an ion exchange resin, etc., if any, can favorably be removed for certain. This may
be applicable either to the recovered TAAH solution or to the photoresist-
containing treated solution, but is preferably applied to the rejuvenated developer
before it is sent to the development step.

Brief Summary Text (72):
Examples of such a <u>membrane</u> treatment unit include a microfiltration <u>membrane</u> unit
wherein use is made of a polyethylene (PE), polypropylene (PP) or
polytetrafluoroethylene (PTFE) <u>membrane</u> filter having micropores of about 0.03 to
1 .mu.m in diameter, and an ultrafiltration <u>membrane</u> unit. A suitable <u>membrane</u>
treatment unit may be chosen and used in accordance with the purpose of treatment.
A nanofilter may alternatively be used instead of the above-mentioned <u>membrane</u>
treatment units.

Detailed Description Text (3):
FIG. 1 is a block diagram of an example of basic equipment for carrying out the
present invention. A development waste from a development unit is once stored in a
development waste tank if necessary, and then sent to a TAAH recovery and refining
unit to obtain a recovered refined TAAH solution, which is then sent to a
rejuvenated developer adjustment unit, wherein the TAAH solution is then mixed with
a surface-active substance such as a surfactant, and replenished and mixed with
(ultra)pure water and/or TAAH (aqueous solution) as needed for adjustment of its
surface-active substance concentration and TAAH concentration to obtain a
rejuvenated developer, which is then sent to the development unit, wherein it is
reused in the development step. Incidentally, virgin TAAH aqueous solution) is
usually used for replenishment, but a TAAH solution recovered and refined in any
other step may instead be used. The excess waste (desalted solution in
electrodialysis or electrolysis, NF concentrate in NF <u>membrane</u> treatment, or the
like) from the TAAH recovery and refining unit is discharged as wastewater via a
wastewater line sometimes together with the excess development waste from the
development waste tank.

Detailed Description Text (4):
FIG. 2 is a block diagram of another example of basic equipment for carrying out
the present invention. A development waste from a development unit is once stored
in a development waste tank if necessary, and part of it is then sent to a TAAH
recovery and refining unit to obtain a recovered refined TAAH solution while
sending other part of it to a photoresist-containing solution tank. If necessary,
that other part of the development waste is mixed with at least part of a
photoresist-containing waste (desalted solution in electrodialysis or electrolysis,
NF concentrate in NF <u>membrane</u> treatment, or the like) recovered from the TAAH
recovery and refining unit. Only the development waste or only the photoresist-
containing waste recovered from the TAAH recovery and refining unit may
alternatively be sent to the photoresist-containing solution tank. The photoresist-
containing solution from the photoresist-containing solution tank is sent as a
source of photoresist as a surface-active substance to a rejuvenated developer
adjustment unit preferably via a cation exchange resin and/or chelate resin
treatment unit, and then mixed there with the recovered refined TAAH solution from
the TAAH recovery and refining unit, and replenished with (ultra)pure water and/or
TAAH (aqueous solution) as needed for adjustment of the photoresist concentration
and TAAH concentration of the mixture to obtain a rejuvenated developer, which is
then sent to the development unit, wherein it is reused in the development step.

Detailed Description Text (5):
In FIG. 2, the "photoresist-containing solution tank" is provided if necessary, and
may be dispensed with. Where the photoresist-containing solution tank is dispensed
with, the development waste in the development waste tank or the waste recovered
from the TAAH recovery and refining unit may be sent to the rejuvenated developer
adjustment unit either directly or via the cation exchange resin and/or chelate

resin treatment unit. Virgin TAAH (aqueous solution) is usually used for
replenishment, but a TAAH solution recovered and refined in any other step may
instead be used. The excess waste (desalted solution in electrodialysis or
electrolysis, NF concentrate in NF membrane treatment, or the like) from the TAAH
recovery and refining unit is discharged as wastewater via a wastewater line
sometimes together with the excess development waste from the development waste
tank and/or the excess photoresist-containing solution from the photoresist-
containing solution tank.

Detailed Description Text (6):
FIG. 3 is a block diagram of still another example of basic equipment for carrying
out the present invention. A development waste from a development unit is once
stored in a development waste tank if necessary, and then sent to a TAAH recovery
and refining unit to obtain a recovered refined TAAH solution, which is then sent
to a rejuvenated developer adjustment unit, wherein the solution is replenished and
mixed with (ultra)pure water and/or TAAH (aqueous solution) as needed for
adjustment of its TAAH concentration to a desired one (about 2.4 wt. % in the case
of TMAH) to obtain a rejuvenated developer. On the other hand, (ultra)pure water
and TAAH (aqueous solution) are mixed with a surface-active substance such as a
surfactant in a developer adjustment unit to obtain a virgin developer having its
TAAH concentration adjusted to a desired one (about 2.4 wt. % in the case of TMAH).
The rejuvenated developer and the virgin developer are sent to a mixer, wherein
they are mixed to obtain an adjusted developer having a desired surface-active
substance concentration, which is then sent to a development unit, wherein it is
used in the development step. Virgin TAAH (aqueous solution) is usually used for
replenishment, but a TAAH solution recovered and refined in any other step may
instead be used. The excess waste (desalted solution in electrodialysis or
electrolysis, NF concentrate in NF membrane treatment, or the like) from the TAAH
recovery and refining unit is discharged as wastewater via a wastewater line
sometimes together with the excess development waste from the development waste
tank.

Detailed Description Text (7):
FIG. 4 is a block diagram of a further example of basic equipment for carrying out
the present invention. A development waste from a development unit is once stored
in a development waste tank if necessary, and part of it is then sent to a TAAH
recovery and refining unit while sending other part of it to a photoresist-
containing solution tank. If necessary, that other part of the development waste is
mixed with at least part of a photoresist-containing waste (desalted solution in
electrodialysis or electrolysis, NF concentrate in NF membrane treatment, or the
like) recovered from the TAAH recovery and refining unit. Only the development
waste or only the photoresist-containing waste recovered from the TAAH recovery and
refining unit may alternatively be sent to the photoresist-containing solution
tank. The photoresist-containing solution from the photoresist-containing solution
tank is sent as a source of photoresist as a surface-active substance to a second
rejuvenated developer adjustment unit preferably via a cation exchange resin and/or
chelate resin treatment unit, and replenished and mixed with (ultra)pure water
and/or TAAH (aqueous solution) as needed for adjustment of its TAAH concentration
to a desired one (about 2.4 wt. % in the case of TMAH) to obtain a second
rejuvenated developer containing the photoresist. On the other hand, a recovered
refined TAAH solution obtained from the TAAH recovery and refining unit is sent to
a first rejuvenated developer adjustment unit, wherein it is then replenished and
mixed with (ultra)pure water and/or TAAH (aqueous solution) as needed for
adjustment of its TAAH concentration to a desired one (about 2.4 wt. % in the case
of TMAH) to obtain a first rejuvenated developer. The first and second rejuvenated
developers are sent to a mixer, wherein they are then mixed to obtain a mixed
rejuvenated developer having a desired photoresist concentration, which is then
sent to a development unit, wherein it is reused in the development step.
Incidentally, the photoresistcontaining solution tank is provided if necessary, and
may be dispensed with like in FIG. 2. Virgin TAAH (aqueous solution) is usually

used for replenishment, but a TAAH solution recovered and refined in any other step may instead be used. The excess waste (desalted solution in electrodialysis or electrolysis, NF concentrate in NF <u>membrane</u> treatment, or the like) from the TAAH recovery and refining unit is discharged as wastewater via a wastewater line sometimes together with the excess development waste from the development waste tank and/or the excess photoresist-containing solution from the photoresist-containing solution tank.

<u>Detailed Description Text</u> (11):
FIG. 7 is a block diagram of an example of basic simple equipment for carrying out the present invention. At least part of a development waste from a development unit is sent to the development waste storage and rejuvenated developer adjustment tank of a rejuvenated developer adjustment unit, from which part of the solution is sent to a TAAH recovery and refining unit. In passing, when an excess of development waste is generated, or when the development waste has a low TAAH concentration, it may be directly discharged as wastewater via a wastewater line, which is, however, not always necessary. A recovered and refined TAAH solution from the TAAH recovery and refining unit may be returned back to the development waste storage and rejuvenated developer adjustment tank, which is supplied with (ultra)pure water and/or TAAH (aqueous solution) as needed for photoresist and TAAH concentrations adjustment to adjust the solution in the tank to a rejuvenated developer, which is then sent to the development unit, wherein it is reused in the development step. At least part of the photoresist-containing waste (e.g., desalted solution in electrodialysis or electrolysis, NF concentrate in NF <u>membrane</u> treatment, or the like) recovered from the TAAH recovery and refining unit may be returned back to the development waste storage and rejuvenated developer adjustment tank preferably via a cation exchange resin and/or chelate resin treatment unit (not shown in the figure). Since the photoresist-containing development waste as a source of surface-active substance flows directly into the development waste storage and rejuvenated developer adjustment tank, however, the foregoing mode may not necessarily be adopted, and the photoresist-containing waste recovered from the TAAH recovery and refining unit may simply be discharged as wastewater via a wastewater line. At a necessary time or if necessary, the excess solution from the development waste storage and rejuvenated developer adjustment tank may be discharged as wastewater via the wastewater line.

<u>Detailed Description Text</u> (17):
TMAH in this development waste as a starting solution was separated, concentrated and recovered into ultrapure water (concentrating liquid) with the electrodialyzer according to a circulation method to obtain a recovered solution. MICRO ACILYZER (registered trademark) G3 manufactured by Asahi Chemical Industry Co., Ltd. was used as the electrodialyzer, wherein use was made of cation exchange <u>membranes</u> ACIPLEX K-501 manufactured by Asahi Chemical Industry Co., Ltd., neutral <u>membranes</u> ACIPLEX PVA #100 manufactured by Asahi Chemical Industry Co., Ltd. instead of anion exchange <u>membranes,</u> and platinum-plated titanium electrodes as both the anode and the cathode.

<u>Detailed Description Text</u> (24):
In rejuvenation treatment of a photoresist development waste for the purpose of obtaining a rejuvenated developer for use in production of, e.g., electronic parts such as semiconductor devices, liquid crystal displays or printed boards, wherein impurities must particularly be avoided, refining treatment steps such as NF <u>membrane</u> separation treatment, electrodialysis and/or electrolysis, ion exchange treatment, and chelate resin contact treatment steps may be properly combined to recover a TAAH solution, which is then mixed with a source of surface-active substance such as a surfactant, a development waste, a photoresist-containing treated solution thereof obtained in NF <u>membrane</u> separation treatment, electrodialysis and/or electrolysis or the like step, or a refined photoresist-containing solution thereof obtained through any refining treatment as needed, whereby a rejuvenated developer having a desired surface tension can be recovered

and reused in the development step.

Hit List

Search Results - Record(s) 1 through 5 of 5 returned.

☐ 1. Document ID: US 6573364 B1

L2: Entry 1 of 5   File: USPT   Jun 3, 2003

US-PAT-NO: 6573364
DOCUMENT-IDENTIFIER: US 6573364 B1

TITLE: Isolation and characterization of Hermansky Pudlak Syndrome (HPS) protein complexes and HPS protein-interacting proteins

DATE-ISSUED: June 3, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Nandabalan; Krishnan	Guilford	CT		
Yang; Meijia	East Lyme	CT		

US-CL-CURRENT: 530/350; 435/317.1

| Full | Title | Citation | Front | Review | Classification | Date | Reference | | | Claims | KWIC | Draw De |

☐ 2. Document ID: US 6488847 B2

L2: Entry 2 of 5   File: USPT   Dec 3, 2002

US-PAT-NO: 6488847
DOCUMENT-IDENTIFIER: US 6488847 B2
** See image for **Certificate of Correction** **

TITLE: Process and equipment for recovering developer from photoresist development waste and reusing it

DATE-ISSUED: December 3, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Sugawara; Hiroshi	Omiya			JP

US-CL-CURRENT: 210/259; 210/143, 210/167, 210/195.1, 210/263, 210/685, 210/96.1, 430/398, 430/399

| Full | Title | Citation | Front | Review | Classification | Date | Reference | | | Claims | KWIC | Draw De |

☐ 3.   Document ID: US 6190556 B1

L2: Entry 3 of 5   File: USPT   Feb 20, 2001

US-PAT-NO: 6190556
DOCUMENT-IDENTIFIER: US 6190556 B1

TITLE: Desalination method and apparatus utilizing nanofiltration and reverse
osmosis membranes

DATE-ISSUED: February 20, 2001

INVENTOR-INFORMATION:
NAME   CITY   STATE   ZIP CODE   COUNTRY
Uhlinger; Robert A.   Carlsbad   CA   92009

US-CL-CURRENT: 210/636; 210/134, 210/195.2, 210/321.64, 210/641, 210/651, 210/652

| Full | Title | Citation | Front | Review | Classification | Date | Reference | | | Claims | KWIC | Draw De |

☐ 4.   Document ID: US 6187519 B1

L2: Entry 4 of 5   File: USPT   Feb 13, 2001

US-PAT-NO: 6187519
DOCUMENT-IDENTIFIER: US 6187519 B1

TITLE: Process and equipment for recovering developer from photoresist development
waste and reusing it

DATE-ISSUED: February 13, 2001

INVENTOR-INFORMATION:
NAME   CITY   STATE   ZIP CODE   COUNTRY
Sugawara; Hiroshi   Omiya   JP

US-CL-CURRENT: 430/399; 430/331, 430/493

| Full | Title | Citation | Front | Review | Classification | Date | Reference | | | Claims | KWIC | Draw De |

☐ 5.   Document ID: US 6083670 A

L2: Entry 5 of 5   File: USPT   Jul 4, 2000

US-PAT-NO: 6083670
DOCUMENT-IDENTIFIER: US 6083670 A

TITLE: Process and equipment for rejuvenation treatment of photoresist development
waste

DATE-ISSUED: July 4, 2000

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Sugawara; Hiroshi	Omiya			JP
Henmi; Hiromi	Kawagoe			JP

US-CL-CURRENT: 430/399

| Full | Title | Citation | Front | Review | Classification | Date | Reference | | | Claims | KWIC | Draw De |

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